**Adsorption of dibutyl phthalate in aqueous solution by mesoporous calcium
silicate grafted non-woven polypropylene**

Xiaohui Wang¹, Kongyin Zhao^{1,2*}, Bingxing Yang^{1*}, Tian Chen², Dongying Li², Hui
Wu³, Junfu Wei¹, Xiaoqing Wu³

¹. State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin
Polytechnic University, Tianjin 300387, China;

². School of Material Science and Engineering, Tianjin Polytechnic University,
Tianjin, 300387, China;

³. School of Textiles, Tianjin Polytechnic University, Tianjin, 300387, China;

*Corresponding author: tjzhaokongyin@163.com, Tel.: +86-2283955362, Fax, +86
-228395055;

Abstract:

The purpose of this research is to synthesize mesoporous calcium silicate grafted
non-woven polypropylene (PP-g-CaSiO₃@SiO₂) and to evaluate its adsorption
performance for dibutyl phthalate (DBP). The morphology, structure and thermal
stability of PP-g-CaSiO₃@SiO₂ were characterized by scanning electron microscope
(SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The
adsorption behavior of PP-g-CaSiO₃@SiO₂ for DBP was investigated and compared
with non-woven polypropylene fabric (PP) and CaSiO₃ grafted PP non-woven
(PP-g-CaSiO₃). The results indicated that the adsorption capacity and adsorption rate
of PP-g-CaSiO₃@SiO₂ were superior to PP and PP-g-CaSiO₃. The adsorption capacity
of DBP by PP-g-CaSiO₃@SiO₂ was 26.68 mg/g, and the adsorption equilibrium time
was two hours. The large surface area and Si-OH groups on PP-g-CaSiO₃@SiO₂
could improve the adsorption capacity and affinity for DBP. Isothermal titration
calorimetry (ITC) was used to illustrate the driving force for the adsorption of DBP to
CaSiO₃@SiO₂. The binding constant K, binding enthalpy (ΔH) and binding entropy
(ΔS) between DBP and CaSiO₃@SiO₂ were obtained to be 7.09×10^5 L/mol, -13.24
 $\times 10^3$ kJ/mol and -3.98 kJ/(K $\cdot$ mol), respectively. The Gibbs' energy change during the
binding process was -33.38 kJ/mol, indicating that the adsorption process was
thermodynamically favorable. Compared with Langmuir model, Freundlich model
was more suitable to describe the adsorption of DBP onto PP-g-CaSiO₃@SiO₂. Lower
temperature and lower pH can promote the adsorption of DBP. PP-g-CaSiO₃@SiO₂
can be recycled for reuse. It is promising to be used as a good adsorption material to

remove DBP or other contaminants from aqueous solutions.

Keywords: Mesoporous SiO₂; DBP adsorption; Calcium silicate; Polypropylene non-woven; Graft; Isothermal titration calorimetry

1. Introduction

Dibutyl phthalate (DBP) has received considerable social attention because of its widespread occurrence as an endocrine disrupting compound (EDC). The adverse effects of DBP are well known as reducing the reproductive ability, decreasing sperm count, raising the incidence of prostate cancer, and causing other reproductive disorders via interaction with the endocrine system^[1,2]. Over past decades, trace-level DBP have been detected in surface water, soil, groundwater, plastic products, and landfill leachates^[3-6]. Consequently, effective treatments are required to eliminate DBP from water^[7].

Several separation processes have been used to remove DBP from water, such as biodegradation^[8], coagulation^[9], enzymatic polymerization^[10] and adsorption^[11]. Among these techniques, adsorption received most researchers' attention because there is no phase change during the removal process^[12,13]. Additionally, the simple fabrication methods and consequent low costs of the adsorbents extend their application range in water treatment.

Many conventional adsorbents^[14-17] showed limited efficiency and capacity when they were used to remove DBP, for example, the activated carbons. The activated carbons are not as effective in polar pollutant removal as in non-polar compounds removal because of their natural properties and non-polar surface^[18,19]. Additionally, the re-collection and regeneration of the activated carbons in the continuous water treatment process are still difficult^[20]. Consequently, it is necessary to find more suitable adsorbents^[21].

Mesoporous silica has attracted great attention due to its high specific surface area, low manufacturing cost, prominent adsorption capacity, and without any secondary pollution. Yu et al^[22] synthesized ordered mesoporous silica materials by a novel route using diatomite as the silica source. The prepared materials possessed regular hexagonal mesoporous structure and high surface area. Regli et al^[23] prepared mesoporous silica encapsulated Si-NCs by dispersing encapsulated Si-NCs within silica shell in aqueous media. The mesoporous silica encapsulated Si-NCs with high

surface area mesoporous is potential to be used as drug delivery agent. The nanoparticles are difficult to be recycled, though they have high adsorption capacity for pollutants. They are commonly mixed with polymers to obtain composite materials. However, the resulting adsorption efficiency will be much compromised because many nanoparticles are agglomerated and entrapped in the polymer matrix [24-26].

Recently, polypropylene (PP) non-woven fabric was utilized in adsorption and filtration process because of its good flexibility, high thermal and chemical stability [27]. Liu et al [12] constructed amphiphilic segments on the surface of polypropylene (PP) non-woven by grafting polymerization using ultraviolet (UV) irradiation. The prepared materials were used to remove endocrine disrupting compounds from aqueous solutions. In our previous research, calcium silicate particles containing mesoporous SiO₂ on the surface (CaSiO₃@SiO₂) were grafted onto polypropylene non-woven fabric [28]. Its adsorption performance for bisphenol A (BPA) was preliminarily investigated. However, the interaction of the endocrine disrupting compounds and PP-g-CaSiO₃@SiO₂ was not clearly explained.

In this research, the PP-g-CaSiO₃@SiO₂ was synthesized for the adsorption of DBP. The adsorption behaviors of DBP were investigated, and the results indicated that the adsorption capacity and adsorption rate were superior to PP and PP-g-CaSiO₃. Its larger specific surface area and the interactions between DBP and Si-OH on PP-g-CaSiO₃@SiO₂ can promote the adsorption. Isothermal titration calorimetry (ITC) was used to illustrate the driving force for the adsorption of DBP to CaSiO₃@SiO₂. The equilibrium adsorption capacity (26.68 mg/g) of PP-g-CaSiO₃@SiO₂ can be reached within 2 h. The PP-g-CaSiO₃@SiO₂ has been proved to be an excellent candidate material to remove DBP from aqueous solutions considering its low cost, fast adsorption rate, and good reusability performance.

2. Experimental

2.1. Materials

Sodium silicate was purchased from Tianjin Jiangtian Chemical Co. Ltd. Calcium chloride was purchased from Tianjin Huazhen Special Chemical Reagent Factory. Acrylic acid (AA), sodium hydroxide (NaOH) and anhydrous ethanol were purchased from Tianjin Second Chemical Reagent Factory. Polypropylene (PP) non-woven was purchased from China Non-woven Co. Ltd. in Xianghe County of Hebei Province. Hydrochloric acid (HCl) was purchased from Tianjin Jiangtian Chemical Co. Ltd.

Dibutyl phthalate (DBP) was purchased from Lianxing Biotechnology Company.

2.2. Preparation of PP-g-CaSiO₃@SiO₃

Polyacrylic acid grafted PP non-woven (PP-g-PAA) was synthesized using reported method^[28]. Sodium polyacrylate grafted PP non-woven (PP-g-COONa) was prepared by neutralizing PP-g-PAA with NaOH. The PP-g-COONa was dipped into 15 wt.% Na₂SiO₃ solution for 0.5 hour, followed by dipping the PP-g-COONa with Na₂SiO₃ solution into 5 wt.% CaCl₂ solution for 3 hours to synthesize CaSiO₃ grafted PP non-woven (PP-g-CaSiO₃). Then the PP-g-CaSiO₃@SiO₂ was produced by acid treatment the PP-g-CaSiO₃ using HCl solution (pH=3). Finally, the resulted PP-g-CaSiO₃@SiO₂ was washed repeatedly with deionized water and dried at 60 °C in vacuum for 24 hours to obtain dried samples. The grafting rate (*G*) of PP non-woven fabric was calculated using the equation below:

$$G (\%) = (W_1 - W_0)/W_0 \times 100\% \quad (1),$$

where *W*₀ and *W*₁ are the weight of the PP non-woven fabric and PP-g-CaSiO₃@SiO₂ or PP-g-CaSiO₃, respectively.

The PP-g-CaSiO₃@SiO₂ and PP-g-CaSiO₃ with the grafting ratio of 31.5±3.5% were selected for characterizations and adsorption tests.

2.3. Characterizations

(1) The surface morphologies of dried PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ were observed using a scanning electron microscope (SEM; S-4800, HITACHI, Japan) after samples were completely dried in vacuum at 60 °C.

(2) The Fourier Transform infrared spectrums (FT-IR) of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ were determined by an AVATAR 330 FT-IR spectrometer (Vector-22, Bruker, Germany).

(3) The X-ray diffraction (XRD) tests of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ were carried out by a Bruker-Axs diffract meter (Germany) with CuKα alpha radiation generated at 40 kV, 30 mA.

(4) A NETZSCH DSC 200 F3 analyzer (NETZSCH, Germany) was used to perform the differential scanning calorimetry (DSC) analysis of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.

2.4. Adsorption of DBP

Batch adsorption experiments of dibutyl phthalate (DBP) were conducted. DBP

was dissolved in ethanol/deionized water solution (the volume ratio of anhydrous ethanol and deionized water was 1:5) to get a 50 mg/L DBP solution. The pH value of DBP solution was set at 3.0 using hydrochloric acid. Then, 0.10 g of PP, PP-g-CaSiO₃ or PP-g-CaSiO₃@SiO₂ was put into 100 mL of above DBP solution in a conical flask. The concentration of DBP was determined by a UV spectrophotometer after sufficient stirring at 298 K in a shaking incubator. The adsorption capacity (Q_t) of DBP was calculated by the equation below:

$$Q_t = (C_0 - C_t) V / m \quad (2),$$

where C_0 and C_t are the concentration of DBP at initial time and time t , respectively. V is the volume of DBP solutions, and m is the mass of adsorbent.

Adsorption isotherm analysis was conducted using DBP solutions (pH = 3.0) of various initial concentrations varying between 10 and 150 mg/L. The DBP solutions with various adsorbents were shaken at 200 r·min⁻¹ for 12 hours at 298 K. The equilibrium adsorption capacities (Q_e) were then determined. The thermodynamic parameters of the adsorption processes were determined at 298 K.

The kinetic adsorption experiments were performed in a conical flask containing 0.10 g of PP, PP-g-CaSiO₃ or PP-g-CaSiO₃@SiO₂ and 100 mL of 50 mg/L DBP solution at 298 K (pH = 3.0). In each adsorption process, the supernatant fluid was taken at regular intervals to determine the concentration of DBP. The adsorption rate constants were calculated using the equation (2).

To investigate the influence of pH value and temperature on the adsorption of DBP, adsorption experiments were performed at various pH values and temperatures. A series of adsorption experiments was performed at 298 K using DBP solutions with pH values ranged from 3.0 to 11.0 to investigate the influence of pH value. HCl and NaOH solutions were used to control the pH values of DBP solutions. The adsorption experiments were conducted at 288 K, 298 K, 308 K, 318 K and 328 K, respectively, to investigate the influence of temperature on the adsorption of DBP. The pH of DBP solution was 3.0.

2.5. ITC characterization of the interactions of DBP and CaSiO₃@SiO₂

The thermodynamics of the interaction between DBP and CaSiO₃@SiO₂ was investigated using a VP-ITC microcalorimeter (MicroCal, Inc., Northampton, MA). The DBP solution (0.179 mM) was used to titrate a suspension of CaSiO₃@SiO₂ (9.65

$\times 10^{-3}$ mg/ml) into the isothermal cell about 28 times in 5 μ l increments at 180 second intervals. The cell temperature was kept at 25°C. In the experiment, an exothermic heat pulse was detected following every injection. Its magnitude decreases gradually until a plateau is reached indicating the saturation of binding. The data was analyzed and the N, enthalpy change (ΔH), and entropy change (ΔS) of the reaction were calculated using the Origin 7.0 based software.

2.6. Reutilization of PP-g-CaSiO₃@SiO₂

The reutilization efficiency of an adsorption material is important. The reutilization efficiency of PP-g-CaSiO₃@SiO₂ was investigated accordingly. The adsorption experiments were performed in a conical flask containing 0.10 g of PP-g-CaSiO₃@SiO₂ and 100 mL of 50 mg/L DBP solution (pH value = 3.0) at 298 K. The PP-g-CaSiO₃@SiO₂ was recovered by rinsing to remove the absorbed DBP on the surface using 100 mL of 0.01 M NaOH solution. Then, the recycled PP-g-CaSiO₃@SiO₂ was reused as the adsorbent of DBP after dried in vacuum at 60 °C for 24 hours. These steps were repeated for five times and the adsorption capacities were recorded.

3. Results and discussion

3.1. Characterizations

3.1.1. SEM

The SEM images of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ are shown in Fig. 1. Compared with the pristine PP fiber, PP-g-CaSiO₃ had thicker diameter, and its surface was rough and rugged. Fig.1 (c) and (d) demonstrate the changes after acid treatment. The mesoporous structure of SiO₂ was produced on the surface of PP-g-CaSiO₃@SiO₂ fibers (Fig. 1(d)) [29]. The particle size of mesoporous calcium silicate was 30-500 nm. As depicted in SEM images, the specific surface area was enhanced significantly due to the mesoporous calcium silicate by making the surface coarser and irregular. It is crucial to the subsequent adsorption process.

Fig. 1.

3.1.2. XRD

The crystal microstructures of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ were investigated by WAXS analysis, as shown in Fig. 2. The 2 θ characteristic peaks of the pure PP are between 20° and 45° region. The same peaks also can be observed in the

WAXS patterns of the PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂. It indicated that the existence of CaSiO₃ did not influence the crystalline form of the PP. After acid modification, a Si-enriched and Ca-depleted surface layer was formed. Consequently, an amorphous hump appeared between 20° and 40° region, as the characteristic peak of hydrated silica ^[29]. This hump was more obvious when PP-g-CaSiO₃ was treated at lower pH value. The spectrum at 2θ=28.8° (320) disappeared after acid modification, which was consistent with the reported results ^[29].

Fig. 2.

3.1.3. DSC

The DSC curves of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ are shown in Fig. 3. PP fiber showed a unique melting peak at 170 °C. Comparatively, there was no obvious endothermic peak in the curve of PP-g-CaSiO₃. It was an indication of the enhanced thermal stability of PP non-woven. There were two peaks in the DSC curve of PP-g-CaSiO₃@SiO₂. They were located around 130 °C and 170 °C, respectively. These two peaks were from the grafted mesoporous silica, indicating the declined thermal stability of PP-g-CaSiO₃ after acid modification.

Fig. 3.

3.2. Adsorption of DBP

3.2.1. Adsorption isotherms

In order to learn more about the adsorption process of DBP at different concentrations, adsorption isotherms of DBP were studied. Fig. 4 depicted the isotherm data of DBP adsorbed on the three materials. The results showed that the equilibrium adsorption capacity (Q_e) increased steadily when the concentration of DBP solution was increased until the saturation adsorption was reached.

The Q_e of PP-g-CaSiO₃@SiO₂ was larger than those of PP-g-CaSiO₃ and PP fabric. The Q_e of PP non-woven for DBP was no more than 10 mg/g. Hydrophobic PP non-woven tends to adsorb DBP which is high hydrophobic and with relatively high log K_{ow} and low water solubility. However, the small specific surface area of PP non-woven limited its adsorption capacity greatly. The adsorption capacity of PP non-woven was improved significantly when its specific surface area was enhanced

by CaSiO₃ grafting modification. PP-g-CaSiO₃@SiO₂ has the highest adsorption capacity with a value of 54.8 mg/g, which can be attributed to its high specific surface area and the abundant Si–OH functional groups formed on the surface after acid treatment. As shown in Fig. 5, hydrogen bonds can be formed between Si–OH group of PP-g-CaSiO₃@SiO₂ and –C=O group of DBP. Additionally, the reactive layer on the PP-g-CaSiO₃@SiO₂ surface formed special porous nanostructure which promoted the adsorption of DBP.

Fig. 4.

Fig. 5.

Langmuir and Freundlich isotherms have been commonly used to describe the adsorption results of organic materials [27, 32].

The Langmuir isotherm is given by the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (3),$$

The Freundlich equation can be expressed as:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (4),$$

where Q_m (mg/g) is the maximum capacity of the adsorbent; Q_e (mg/g) is the amount of adsorption at equilibrium; C_e is the equilibrium concentration of DBP (mg/L); K_F (L/g) is the Freundlich adsorption coefficient; K_L (L/mg) is the Langmuir constant related to the affinity of binding sites; and n is the Freundlich exponent obtained from the liquid phase adsorption isotherm.

The Langmuir and Freundlich isotherm constants were determined from the plots of C_e/Q_e versus C_e , and $\lg Q_e$ versus $\lg C_e$, respectively, as shown in Fig. 6. The isotherm constants and the linear regression coefficients obtained from the experimental data were presented in Table 1.

Fig. 6.

Table 1

According to the linear regression constant R^2 in Table 1, the adsorption of DBP

correlated better with the Freundlich equation than the Langmuir equation in the studied concentration range when PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ were used as the adsorbents. Based on the former research^[12], Freundlich model is an empirical equation of a multilayer adsorption process on a heterogeneous surface. Consequently, the adsorptions of DBP on PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ should be multilayer adsorption processes. The multilayer adsorption behaviors of these two materials could come from the mesoporous structures of their surface. The adsorption of DBP by PP correlated better with the Langmuir equation because the surface of PP was smooth.

As the fitting results showed, the maximum adsorption capacity (Q_m) of DBP on PP-g-CaSiO₃@SiO₂ was 166.4 mg/g, which was much higher than those of PP and PP-g-CaSiO₃. It is a solid evidence of the successful improvement of the adsorption capacity by grafting CaSiO₃@SiO₂ on PP.

3.2.2. Thermodynamic characterization of the DBP–CaSiO₃@SiO₂ interactions

ITC results could illustrate the mechanism of the interaction between DBP and CaSiO₃@SiO₂. The upper section of Fig. 7 represents the raw data as supplied by the instrument and the progression of the experiment in time. The lower part of Fig. 7 shows the titration curve, resulting from the integration of the individual peaks and plotted as ΔH in kcal/mol against the molar ratio DBP/CaSiO₃@SiO₂. From Fig. 7, the released heat was detected after each titration of DBP into CaSiO₃@SiO₂. The binding constant K , binding enthalpy (ΔH) and binding entropy (ΔS) between DBP and CaSiO₃@SiO₂ was 7.09×10^5 L/mol, -13.24×10^3 kJ/mol and -3.98 kJ/(K*mol), respectively. The Gibbs' energy change during the binding process was calculated to be -33.38 kJ/mol from the equation $\Delta G = -RT \ln K$. This indicated that the adsorption process was thermodynamically favorable, and the DBP was adsorbed to the CaSiO₃@SiO₂ via H-bonds between C=O of DBP and HO-Si of CaSiO₃@SiO₂. The reaction is exothermic, therefore, high temperatures will not in favor of forming the hydrogen bonds. The findings agreed well with the temperature effects on the adsorption of DBP.

Fig. 7.

3.2.3. Adsorption kinetics

The influence of contact time on the adsorption capacity of DBP by PP,

PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂ is presented in Fig. 8. As seen from the figure, the adsorption capacity of PP-g-CaSiO₃@SiO₂ (Q_t) increased significantly when the contact time t increased. PP-g-CaSiO₃@SiO₂ displayed excellent adsorption performance. Its adsorption rate was fast and the adsorption process reached the equilibrium in about 2 h. Both the Q_t and the adsorption rate of PP-g-CaSiO₃@SiO₂ were better than those of PP and PP-g-CaSiO₃.

Fig. 8.

Two kinetic models were used to investigate the adsorption processes of DBP, including pseudo-first-order and pseudo-second-order. Lagergren pseudo-first-order and pseudo-second-order models are the most commonly used adsorption rate equations. The pseudo-first-order kinetic model is expressed by the following equation^[30]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

The pseudo-second-order kinetic model is represented as^[31]:

$$t/Q_t = 1/(K_2 Q_e^2) + t/Q_e \quad (5),$$

where k_1 and k_2 are the rate constants of the first-order and second-order adsorptions. Q_e and Q_t are adsorption quantity of DBP at the equilibrium and at time t , respectively. The slope and the intercept of the plot of $\ln(Q_e - Q_t)$ against t and t/Q_t versus t were used to calculate the k_1 and k_2 , respectively.

Fig. 9 shows the fitting curves of the two kinetics models. The fitting results are listed in Table 2. As seen from the linear regression coefficients (R^2), the adsorption of DBP was better described by the pseudo-second order model.

Fig. 9.

Table 2

3.2.4. Influence of temperature on the adsorption of DBP

The effects of temperature on the Q_e of DBP on PP-g-CaSiO₃@SiO₂ fabric are shown in Fig. 10. The adsorption was significantly influenced by the temperature ranged from 288 to 328 K. The Q_e decreased as the temperature increased. The highest adsorption capacity appeared at 288 K in our study range. It indicated that low

temperature can promote the adsorption because the adsorption reaction is an exothermal process. When the adsorption was conducted at room temperature (298 K), the adsorption capacity of PP-g-CaSiO₃@SiO₂ was 56.33 mg/g.

Fig. 10.

3.2.5. Influence of pH on the adsorption of DBP

To investigate the influence of pH value on the adsorption capacity of DBP, a series of experiments was conducted at various pH values ranged from 3.0 to 11.0. The results are shown in Fig. 12. The equilibrium adsorption capacity (Q_e) decreased when the pH value increased from 3.0 to 11.0. In the adsorption process, the pH value of the DBP solution was an important factor because it can influence the properties of PP-g-CaSiO₃@SiO₂ surface and the properties of contaminants^[32], such as polarity, hydrophobicity. When pH value is less than 7, DBP can be hydrolyzed to phthalic acid with strong polarity (refer to Fig. 11 a). Consequently, the hydrogen bonding interactions became stronger in the system. On the other hand, the isoelectric point of the mesoporous SiO₂ sample is about 2.0. It means that the mesoporous surface will be negatively charged when pH>2.0. A higher pH value above 2.0 will make the mesoporous surface negatively charged more. Furthermore, the DBP will be hydrolyzed (see Fig. 11 b) when pH value increased above 7.0. The consequent increased electrostatic repulsion between the DBP and PP-g-CaSiO₃@SiO₂ surface made Q_m decreased.

Fig. 11.

Fig. 12.

3.2.6. Reutilization of PP-g-CaSiO₃@SiO₂ for the adsorption of DBP

Fig. 13 shows the reusability performance of PP-g-CaSiO₃@SiO₂ for the adsorption of DBP, which was investigated by repeating the adsorption/desorption process for 5 times. As seen from the results, over 80% of the Q_e can be recovered by washing for the next adsorption process. The decrease of Q_e can be ascribed to the loss of the active mesoporous SiO₂ sites on the fiber surface during the repeated processes. The experimental results proved high recycle performance of PP-g-CaSiO₃@SiO₂, which

made it promising in the applications of DBP removal.

Fig. 13.

3.2.7. Comparison with other reported adsorbents

We have summarized the key properties of other reported DBP adsorbents^[32-37] and our PP-g-CaSiO₃@SiO₂ for comparison. These data are given in Table 3. The equilibrium adsorption capacity (Q_e) obtained in our work is medium among all the reported works, while the equilibrium time (T_e) of PP-g-CaSiO₃@SiO₂ is the shortest, which is 2 h only. If Q_e/T_e was used to describe the adsorption efficiency, we can understand better about the performance of each material, because it means the average adsorption quantity per unit time. It is found that our PP-g-CaSiO₃@SiO₂ has the highest Q_e/T_e value. It would be a good advantage. Additionally, the low-cost, availability and reusability of the PP-g-CaSiO₃@SiO₂ made it better than other materials in practical applications.

Table 3

4. Conclusion

PP non-woven grafted calcium silicate containing mesoporous SiO₂ (PP-g-CaSiO₃@SiO₂) was synthesized by Ca²⁺ cross-linking and acid modification. Compared with the PP-g-CaSiO₃ and PP, PP-g-CaSiO₃@SiO₂ possessed better adsorption properties for DBP. Adsorption isotherms and kinetics indicated that the large surface area and Si-OH groups on PP-g-CaSiO₃@SiO₂ can improve the adsorption capacity and the affinity for DBP. In isotherm analysis, the adsorption of DBP on fabrics was a multilayer adsorption, and the Freundlich model matched better for the adsorption performance than the Langmuir model. For adsorption kinetic analysis, the pseudo-second-order kinetic model provided a better explanation than the pseudo-first-order kinetic model. Low temperature and low pH value can promote the adsorption of DBP. ITC could be used to illustrate the driving force for the adsorption of DBP to CaSiO₃@SiO₂. The binding constant K, binding enthalpy (ΔH) and binding entropy (ΔS) between DBP and CaSiO₃@SiO₂ was 7.09×10^5 L/mol, -13.24×10^3 kJ/mol and -3.98 kJ/(K*mol), respectively. The Gibbs' energy change during the binding process was -33.38 kJ/mol, indicating that the adsorption process

was thermodynamically favorable. The processing method and recycling technique of PP-g-CaSiO₃@SiO₂ non-woven is simple, low cost, and free of pollutants. This work provided a valuable functional fiber material that could be further applied in the elimination of DBP and other endocrine disrupting compounds (EDCs) from water.

Acknowledgments

The research is supported by National Science Foundation of China (51103102, 21504063, 41301542), Tianjin Science Technology Research Funds of China (12JCYBJC3200, 15JCQNJC08900, 13ZDSF00100), and the Science and Technology Plans of Tianjin (15PTSJYC00240).

Reference:

- [1] O.T. Komesli, M. Muz, M.S. Ak, S. Bakirdere, C.F. Gokcay, Occurrence, fate and removal of endocrine disrupting compounds (EDCs) in Turkish wastewater treatment plants, *Chemical Engineering Journal* 277 (2015) 202-208.
- [2] O. Bechambi, M. Chalbi, W. Najjar, S. Sayadi, Photocatalytic activity of ZnO doped with Ag on the degradation of endocrine disrupting under UV irradiation and the investigation of its antibacterial activity, *Applied Surface Science* 347 (2015) 414-420.
- [3] A.D. Vethaak, J. Lahr, S.M. Schrap, A.C. Belfroid, G.B.J. Rijs, A. Gerritsen, J. de Boer, A.S. Bulder, G.C.M. Grinwis, R.V. Kuiper, J. Legler, T.A.J. Murk, W. Peijnenburg, H.J.M. Verhaar, P. de Voogt, An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands, *Chemosphere* 59 (2005) 511-524.
- [4] M.J. Benotti, R.A. Trenholm, B.J. Vanderford, J.C. Holady, B.D. Stanford, S.A. Snyder, Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water, *Environmental Science & Technology* 43 (2009) 597-603.
- [5] Y. Yoon, J. Ryu, J. Oh, B.-G. Choi, S.A. Snyder, Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea), *Science of The Total Environment* 408 (2010) 636-643.
- [6] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance,

Environmental Science & Technology 36 (2002) 1202-1211.

- [7] A.R. Reis, K. Tabei, Y. Sakakibara, Oxidation mechanism and overall removal rates of endocrine disrupting chemicals by aquatic plants, *Journal of Hazardous Materials* 265 (2014) 79-88.
- [8] C. Barbeau, L. Deschênes, D. Karamanev, Y. Comeau, R. Samson, Bioremediation of pentachlorophenol-contaminated soil by bioaugmentation using activated soil, *Applied Microbiology and Biotechnology* 48 (1997) 745-752.
- [9] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, *Water Research* 41 (2007) 1013-1021.
- [10] I.D. Buchanan, J.A. Nicell, Model development for horseradish peroxidase catalyzed removal of aqueous phenol, *Biotechnology and Bioengineering* 54 (1997) 251-261.
- [11] C. Jung, J. Heo, J. Han, N. Her, S.J. Lee, J. Oh, J. Ryu, Y. Yoon, Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, *Separation and Purification Technology* 106 (2013) 63-71.
- [12] K. Liu, J.F. Wei, X.Y. Zhou, N. Liu, Construction of amphiphilic segments on polypropylene non-woven surface and its application in removal of endocrine disrupting compounds (EDCs) from aqueous solution, *Applied Surface Science* 337 (2015) 178-187.
- [13] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, *Desalination* 202 (2007) 156-181.
- [14] J.L. Sotelo, G. Ovejero, A. Rodríguez, S. Álvarez, J. Galán, J. García, Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon, *Chemical Engineering Journal* 240 (2014) 443-453.
- [15] R. Toor, M. Mohseni, UV-H₂O₂ based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water, *Chemosphere* 66 (2007) 2087-2095.
- [16] Z. Yu, S. Peldszus, P.M. Huck, Adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon. 1. adsorption capacity and kinetics, *Environmental Science & Technology* 43 (2009)

1467-1473.

- [17] N.A. Khan, B.K. Jung, Z. Hasan, S.H. Jhung, Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and metal–organic frameworks, *Journal of Hazardous Materials* 282 (2015) 194-200.
- [18] Z. Yu, S. Peldszus, P.M. Huck, Adsorption characteristics of selected pharmaceuticals and an endocrine disrupting compound—Naproxen, carbamazepine and nonylphenol—on activated carbon, *Water Research* 42 (2008) 2873-2882.
- [19] C. Moreno-Castilla, M.A. Ferro-Garcia, J.P. Joly, I. Bautista-Toledo, F. Carrasco-Marin, J. Rivera-Utrilla, Activated carbon surface modifications by nitric acid, hydrogen peroxide, and ammonium peroxydisulfate treatments, *Langmuir* 11 (1995) 4386-4392.
- [20] M.K. Purkait, A. Maiti, S. DasGupta, S. De, Removal of congo red using activated carbon and its regeneration, *Journal of Hazardous Materials* 145 (2007) 287-295.
- [21] M. Julinová, R. Slavík, Removal of phthalates from aqueous solution by different adsorbents: A short review, *Journal of Environmental Management* 94 (2012) 13-24.
- [22] Z. Yu, Y. Wang, X. Liu, J. Sun, G. Sha, J. Yang, C. Meng, A novel pathway for the synthesis of ordered mesoporous silica from diatomite, *Materials Letters* 119 (2014) 150-153.
- [23] S. Regli, J.A. Kelly, M.A. Barnes, C.M. Andrei, J.G.C. Veinot, Mesoporous silica encapsulation of silicon nanocrystals: Synthesis, aqueous dispersibility and drug release, *Materials Letters* 115 (2014) 21-24.
- [24] L.T. Yan, H.G. Schoberth, A. Böker, Lamellar microstructure and dynamic behavior of diblock copolymer/nanoparticle composites under electric fields, *Soft Matter* 6 (2010) 5956-5964.
- [25] K. Xu, R. Guo, B. Dong, L.T. Yan, Directed self-assembly of Janus nanorods in binary polymer mixture: towards precise control of nanorod orientation relative to interface, *Soft Matter* 8 (2012) 9581-9588.
- [26] R. Guo, Z. Liu, X.M. Xie, L.T. Yan, Harnessing Dynamic Covalent Bonds in Patchy Nanoparticles: Creating Shape-Shifting Building Blocks for Rational and Responsive Self-Assembly, *The Journal of Physical Chemistry Letters* 4 (2013) 1221-1226.

- [27] K.Y. Zhao, B.B. Lin, W.K. Cui, L.Z. Feng, T. Chen, J.F. Wei, Preparation and adsorption of bovine serum albumin-imprinted polyacrylamide hydrogel membrane grafted on non-woven polypropylene, *Talanta* 121 (2014) 256-262.
- [28] K.Y. Zhao, T. Chen, D.Y. Li, X.X. Zhang, H.Y. Song, J.F. Wei, Preparation and characterization of mesoporous calcium silicate grafted polypropylene non-woven fabric, *Materials Letters* 141 (2015) 110-113.
- [29] W. Xue, A. Bandyopadhyay, S. Bose, Mesoporous calcium silicate for controlled release of bovine serum albumin protein, *Acta Biomaterialia* 5 (2009) 1686-1696.
- [30] E. Tütem, R. Apak, Ç.F. Ünal, Adsorptive removal of chlorophenols from water by bituminous shale, *Water Research* 32 (1998) 2315-2324.
- [31] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Research* 34 (2000) 735-742.
- [32] X.Y. Zhou, J.F. Wei, H. Zhang, K. Liu, H. Wang, Adsorption of phthalic acid esters (PAEs) by amphiphilic polypropylene non-woven from aqueous solution: The study of hydrophilic and hydrophobic microdomain, *Journal of Hazardous Materials* 273 (2014) 61-69.
- [33] Z.Q. Fang, H.J. Huang, Adsorption of dinbutyl phthalate onto nutshell based activated carbon. Equilibrium, kinetics and thermodynamics, *Adsorption Science & Technology* 27 (2009) 685-700.
- [34] S. Murai, S. S. Imajo, Y. S. H. Takasu, K. K. Takahashi, K. j. Hattori, Removal of phthalic acid esters from aqueous solution by inclusion and adsorption on β -cyclodextrin, *Environmental Science & Technology* 32 (1998) 782-787.
- [35] C.Y. Chen, Y.C. Chung, Removal of phthalate esters from aqueous solutions by chitosan bead, *Journal of Environmental Science and Health-Part A Toxic/Hazardous Substances and Environmental Engineering* 41 (2006) 235-248.
- [36] C.Y. Chen, C.C. Chen, Y.C. Chung, Removal of phthalate esters by α -cyclodextrin-linked chitosan bead, *Bioresource Technology* 98 (2007) 2578-2583.
- [37] H.H.P. Fang, H.H. Zheng, Adsorption of phthalates by activated sludge and its biopolymers, *Environmental Technology* 25 (2004) 757-761.

List of Figures

- Fig. 1.** SEM images of (a) PP, (b) PP-g-CaSiO₃, and (c, d) PP-g-CaSiO₃@SiO₂.
- Fig. 2.** XRD curves of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.
- Fig. 3.** The DSC curves of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.
- Fig. 4.** The isothermal adsorption curves of DBP by PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂. Adsorption condition: pH value of DBP solution 3.0, temperature 298 K.
- Fig. 5.** The schematic of hydrogen bonding between PP-g-CaSiO₃@SiO₂ and DBP.
- Fig. 6.** Fitting curves of Langmuir model (a) and Freundlich model (b).
- Fig. 7.** ITC data curves for the titration of a 0.179 mM DBP solution into a dispersion of CaSiO₃@SiO₂ (9.65×10^{-3} mg/ml) at 25°C.
- Fig. 8.** The kinetic adsorption curves of DBP by PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂. Adsorption condition: pH value of DBP solution 3.0, temperature 298 K, $C_0=50$ mg/L.
- Fig. 9.** Fitting curves of pseudo-first order kinetic model (a) and pseudo-second order kinetic model (b).
- Fig. 10.** The Q_e of DBP on PP-g-CaSiO₃@SiO₂ fiber under various concentrations and temperatures. The pH value of DBP solution was 3.0.
- Fig. 11.** Dissociation of DBP in (a) acid and (b) alkaline condition.
- Fig. 12.** The effect of pH values on the Q_e of DBP using PP-g-CaSiO₃@SiO₂ as adsorbent. Adsorption condition: temperature 298 K, $C_0=50$ mg/L.
- Fig. 13.** Reusability of PP-g-CaSiO₃@SiO₂ for the adsorption of DBP.
Adsorption condition: pH value of DBP solution 3.0, temperature 298 K, $C_0=50$ mg/L.

Fig. 1. SEM images of (a) PP, (b) PP-g-CaSiO₃, and (c, d) PP-g-CaSiO₃@SiO₂.

Fig. 2. XRD curves of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.

Fig. 3. The DSC curves of PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.

Fig. 4. The isothermal adsorption curves of DBP by PP, PP-g-CaSiO₃ and PP-g-CaSiO₃@SiO₂.

Adsorption condition: pH value of DBP solution 3.0, temperature 298 K.

598

599

600

601

Fig. 5. The schematic of hydrogen bonding between PP-g-CaSiO₃@SiO₂ and DBP.

602

603

604

605

Fig. 6. Fitting curves of Langmuir model (a) and Freundlich model (b).

Fig. 7. ITC data curves for the titration of a 0.179 mM DBP solution into a dispersion of $\text{CaSiO}_3\text{@SiO}_2$ (9.65×10^{-3} mg/ml) at 25°C

Fig. 8. The kinetic adsorption curves of DBP by PP, PP-g- CaSiO_3 and PP-g- $\text{CaSiO}_3\text{@SiO}_2$. Adsorption condition: pH value of DBP solution 3.0, temperature 298 K, $C_0=50$ mg/L.

(a) Pseudo-first order kinetic model (b) Pseudo-second order kinetic model
Fig. 9. Fitting curves of pseudo-first order kinetic model (a) and pseudo-second order kinetic model (b).

Fig. 10. The Q_e of DBP on PP-g-CaSiO₃@SiO₂ fiber under various concentrations and temperatures. The pH value of DBP solution was 3.0.

Fig. 11. Dissociation of DBP in (a) acid and (b) alkaline condition.

Fig. 12. The effect of pH values on the Q_e of DBP using PP-g-CaSiO₃@SiO₂ as adsorbent.

Adsorption condition: temperature 298 K, $C_0=50$ mg/L.

Fig. 13. Reusability of PP-g-CaSiO₃@SiO₂ for the adsorption of DBP.

Adsorption condition: pH value of DBP solution 3.0, temperature 298 K, $C_0=50$ mg/L.

List of Tables:

Table 1. Langmuir and Freundlich adsorption isotherm parameters.

Table 2. Kinetic parameters fitted to pseudo-first-order model and pseudo-second-order kinetics model.

Table 3. Comparison of the published materials and the PP-g-CaSiO₃@SiO₂

Table 1 Langmuir and Freundlich adsorption isotherm parameters.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	$Q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R^2	K_F	$1/n$	R^2
PP	23.79	0.0018	0.9666	0.3083	0.8228	0.9739
PP-g-CaSiO ₃	130.70	0.0023	0.7852	0.3329	0.9446	0.9968
PP-g-CaSiO ₃ @SiO ₂	166.40	0.0057	0.7836	1.0192	0.9172	0.9867

Table 2 Kinetic parameters fitted to pseudo-first-order model and pseudo-second-order kinetic model.

Adsorbent	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	$Q_e(\text{mg/g})$	$k_1(\text{h}\cdot\text{mg/g})$	R^2	$Q_e(\text{mg/g})$	$k_2(\text{h}\cdot\text{mg/g})$	R^2
PP	3.84	0.2126	0.9770	3.33	7.5208	0.9998
PP-g-CaSiO ₃	12.76	0.6074	0.9374	11.83	2.8345	0.9998
PP-g-CaSiO ₃ @SiO ₂	25.02	0.7443	0.9223	26.68	0.2122	0.9989

Table 3 Comparison of the published materials and the PP-g-CaSiO₃@SiO₂

	Adsorbent	$T_e(\text{h})$	Q_e/T_e	Reference
	$Q_e(\text{mg/g})$		$(\text{mg/g}\cdot\text{h})$	
PP-g-SA-HEA	33.0	4.0	8.25	[12]
PP-g-GAM-OA	28.41	10	2.84	[32]
Nutshell-based activated carbon	50.73	30	1.69	[33]
β -cyclodextrin	1.39	5.0	0.28	[34]
Chitosan bead	0.54	6.0	0.09	[35]
β -cyclodextrin-linked chitosan bead	3.16	6.0	0.53	[36]
Activated sludge	0.206	24	0.01	[37]
PP-g-CaSiO ₃ @SiO ₂	26.68	2.0	13.34	This work

List of Suggested Reviewers

1. Chao Liu

School of Materials Science and Engineering, Hebei University of Technology,
Tianjin 300130, PR China

Phone: +86 22-60204805 fax: +86 22-60204805

Email: liuchao@hebut.edu.cn

He is an expert for the preparation of mesoporous or microporous nanomaterials and published some papers.

2. Litang yan

Institute of Polymer Science & Technology, Department of Chemical Engineering,
Tsinghua University, Qinghuayuan, Haidian, 100084 Beijing, China

Phone: +86 10 62797263 fax: +86 10 62784550

Email: ltyan@mail.tsinghua.edu.cn

He is an expert in the chemical engineering and nano materials.

3. Okan Tarık Komesli

Ataturk University, Department of Environmental Engineering, 25250 Erzurum,
Turkey

Phone: +90 312 210 58 65.

Email: okan.komesli@gmail.com

He is an expert in the environmental engineering.

Graphical Abstract

The schematic of hydrogen bonding for DBP binding to PP-g-CaSiO₃@SiO₂.